

CAMERE PROCESS FOR CARBON DIOXIDE HYDROGENATION TO FORM METHANOL

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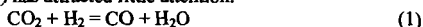
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INTRODUCTION

Catalytic hydrogenation of CO₂ has been one of major approaches to diminish the greenhouse gas because large amounts of CO₂ can be converted to resources such as methanol and other oxygenates compounds by the reaction. However, a direct hydrogenation of CO₂ shows low conversion, which increases the recycle gas to obtain high methanol productivity. CAMERE process (Scheme 1) has been developed to form methanol from CO₂ via a reverse-water-gas-shift reaction (1). In the CAMERE process, carbon dioxide is converted to CO and H₂O by the reverse-water-gas-shift reaction (RWReaction) and then, the produced gas (CO/CO₂/H₂) is fed to the methanol reactor after removing the water. Each reactor in the process has the recycle stream to increase CO₂ conversion to CO and carbon oxide (CO₂+CO) conversion to methanol, respectively. With the gas feeding of CO/CO₂/H₂, the water produced in the methanol reactor is chemically eliminated through a water-gas-shift reaction, increasing carbon oxide conversion to methanol and then decreasing the recycle gas in the methanol reactor. The methanol productivity in the CAMERE process depends on the CO concentration in the feed gas of the methanol reactor, which is dependent on the RWReaction conditions, especially the temperature.

A water-gas-shift reaction has been studied intensively for the last several decades in order to adjust for H₂/CO ratio in the synthesis gas (2-4). On the contrary, a reverse- water-gas-shift reaction of Eq.(1) has attracted little attention.



Besides, all the kinetic equations published on the RWReaction have been obtained over copper-containing catalysts at low temperatures (5-7). Therefore, we need to develop a mathematical model for the RWReaction at high temperature to predict the effects of operating condition changes of the RWReactor on the overall performance of the CAMERE process. A mathematical form based on a redox mechanism is obtained over Fe₂O₃/Cr₂O₃ catalyst at 773 K. Apparent activation energy for the RWReaction is calculated from an arrhenius plot of specific activities acquired over the temperature of 673-823 K, which is 109.8 kJ/mol. The CAMERE process has been evaluated based on the kinetic equation of the RWReaction to find an optimum operating condition to form methanol from CO₂.

EXPERIMENTAL

A commercial Fe₂O₃/Cr₂O₃(Fe:Cr=9:1 in molar ratio) catalyst was investigated to obtain a kinetic equation for the RWReaction over the temperature of 593-723 K. The catalyst charged in a tubular catalytic reactor is heated up to a reaction temperature in the presence of CO₂ and H₂ before the RWReaction. The RWReactions are performed under the reaction conditions of 1atm, temperature of 670-823 K, and W/F (g_{cat}.h/mol of CO₂ in the feed) of 0.05-3.7. The absence of diffusion limitations is confirmed by changing the size and the amount of the catalyst.

RESULTS AND DISCUSSION

The RWReaction is endothermic, and hence conversion of CO₂ is favored by high reaction temperature. Hence the RWReaction should be operated at high temperature above 773 K to keep CO₂ conversion up to 60%, increasing carbon oxide conversion to methanol in the second step of the CAMERE process. The kinetic studies for the RWReaction are performed in an integral plug flow reactor over Fe₂O₃/Cr₂O₃ catalyst at 773 K. A redox mechanism is derived from the best fitting of the experimental data. The surface of the Fe₂O₃/Cr₂O₃ catalyst is successively oxidized by CO₂ and reduced by H₂ by the redox mechanism. For the redox mechanism a rate expression is derived from that the step, which the catalyst surface was reduced by H₂, is a rate-determining step. The kinetic equation is expressed as follows;

$$r = \frac{P_{\text{CO}_2} P_{\text{H}_2} / P_{\text{CO}} - P_{\text{H}_2\text{O}} / K}{1/kK_1 + P_{\text{CO}_2}/kP_{\text{CO}}}$$

where, k = apparent rate constant of the RWReaction (mol h⁻¹ g_{cat}⁻¹ atm⁻¹)

K = equilibrium constant of the RWReaction (dimensionless)

K_1 = equilibrium constant of the surface oxidation step by CO₂ (dimensionless)

r = reaction rate (mol h⁻¹ g_{cat}⁻¹), P_i = partial pressure of i component (atm)

Overall apparent activation energy can be determined from the effect of temperature on the rate for the RWReaction at a constant composition. Hence the RWReaction is performed with

temperature over the W/F ($g_{cat}/h/mol$ of CO_2 in the feed) of 0.05-1.5. Figure 1 gives the experimental data and the values calculated from the kinetic equation for the RWReaction. An arrhenius type plot of $\ln(\text{rate})$ versus $1/T$ is obtained from CO_2 conversion with the reaction temperature. Figure 2 shows the activation energy of 109.77 kJ/mol for the RWReaction. The activation energy is similar to that of copper-containing catalyst (8).

The CAMERE process has been simulated based on the kinetic equation of the RWReaction and carbon oxide conversion to methanol to compare the operating conditions of the CAMERE process with those of a direct CO_2 hydrogenation. We use the published results on the carbon oxide conversion to methanol under the reaction conditions of 50 atm and 523 K (9-10). Table 1 shows the simulation results that are dependent on the presence and conditions of the RWReaction. The same amount (14.3 kgmol/hr) of CO_2 and H_2 is fed to the direct CO_2 hydrogenation and CAMERE process, respectively. In the methanol reactor the recycle gas is calculated by subtracting the purge gas (=P) from the downstream gas (=F2). To obtain methanol productivity of 2 kg mol/h, the gas of 42.82 kgmol/h should be recycled in the direct CO_2 hydrogenation process. On the other hand, the gas of 16.27 kgmol/h is recycled in the CAMERE process to form methanol of 2.06 kgmol/h where there is no recycle step in the RWReactor ($R1=0$). Moreover, the recycle gas is further reduced to 10.66 kgmol/h when the recycle ratio is the one in the RWReactor ($R1=1$). It means that the recycle gas for the same methanol production strongly depends on the CO concentration in the feed gas of the methanol reactor (F1). The CO concentration is decided by the presence of the RWReaction and the recycle ratio ($R1$). The CO concentration in the F1 stream increases when the temperature and recycle ratio of the RWReaction is increased. With the elimination of water by the RWReaction, the recycle gas of the CAMERE process is minimized compared with the direct CO_2 hydrogenation process to form the same amount of methanol. Therefore, the reactor size to obtain methanol of 2 kgmol/h in the CAMERE process can be decreased up to one fourth of the one of the direct CO_2 hydrogenation process when the product gas of 50% in the RWReactor is recycled. Table 1 indicates the relationships between CO concentrations in the feed gas with the recycle gas for the same methanol production. The water produced in direct CO_2 hydrogenation process is comparable with that in the methanol reactor of the CAMERE process, that are 2.31 kgmol/h in the direct process and 0.34 kgmol/h in the CAMERE process ($R1=1$) for the same methanol production of 2.0 kgmol/h, respectively. The pilot plant for methanol production of 5 kg/day is constructed in our laboratory.

CONCLUSIONS

A rate equation for a reverse-water-gas-shift reaction is obtained based on a redox mechanism over Fe_2O_3/Cr_2O_3 catalyst at 773 K, which apparent activation energy is 109.8 kJ/mol. The CAMERE process has been simulated based on the kinetic equation of the RWReaction and carbon oxide conversion to methanol to find an optimum operating conditions to form methanol from CO_2 . With the elimination of water by the RWReaction, the recycled gas in the CAMERE process is decreased more than four times compared with a direct CO_2 hydrogenation for the same methanol production.

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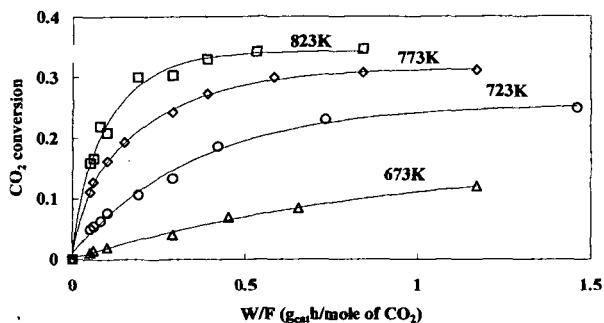


Figure 1. CO₂ conversion with reaction temperature over Fe₂O₃/Cr₂O₃ with the H₂/CO ratio of 1. The marks are experimental points; the lines are calculated values from the kinetic equation.

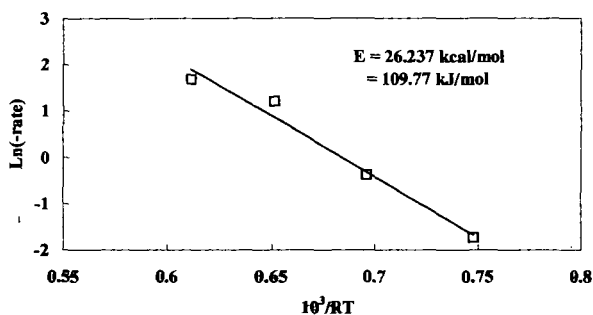
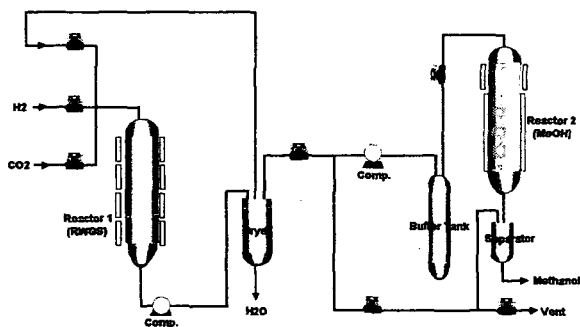


Figure 2. Arrhenius plot of specific activities for the continuous flow reaction of CO₂/H₂ of 1 over Fe₂O₃/Cr₂O₃ catalyst.



Scheme 1. CAMERE process diagram for MeOH of 5 kg/day from CO₂

Table 1. Comparison of the CAMERE process with a direct CO₂ hydrogenation.

Process	A1	R1	A2	R2	F1	F2	L1	L2	MeOH Yield	P
Direct CO ₂ Hydrogenation Process	-	-	1.0	0	14.3	11.7	1.47	0.57	16.04	11.7
	-	-	0.9481	1	24.3	20.4	2.23	0.94	26.32	10.2
	-	-	0.9243	2	32.5	27.2	2.78	1.22	34.12	9.08
	-	-	0.9100	3	38.9	32.8	3.21	1.44	40.31	8.20
	-	-	0.9003	4	44.3	37.5	3.56	1.62	45.35	7.49
	-	-	0.8930	5	48.8	41.4	3.85	1.77	49.54	6.90
	-	-	0.8874	6	52.7	44.8	4.10	1.90	53.10	6.40
	-	-	0.8829	7	56.2	47.8	4.31	2.00	56.16	5.98
	-	-	0.8790	8	59.2	50.5	4.49	2.10	58.82	5.61
CAMERE Process	0.3978	0	0.3978	0	12.2	8.66	1.30	1.10	30.80	8.66
	0.3978	0	0.4636	1	19.3	14.2	1.91	1.57	43.97	7.10
	0.3978	0	0.5050	2	24.2	18.4	2.32	1.86	51.92	6.13
	0.3978	0	0.5324	3	28.4	21.7	2.62	2.06	57.52	5.43
	0.3978	0	0.5514	4	31.7	24.4	2.85	2.21	61.81	4.89
	0.3978	0	0.5652	5	34.5	26.7	3.05	2.33	65.23	4.45
	0.3978	0	0.5753	6	36.7	28.6	3.21	2.43	68.05	4.08
	0.3978	0	0.5832	7	38.6	30.2	3.35	2.52	70.41	3.78
	0.3978	0	0.5893	8	40.3	31.6	3.46	2.59	72.43	3.52
	0.2906	1	0.2906	0	11.8	7.93	1.38	1.23	34.42	7.93
	0.2906	1	0.3487	1	18.1	12.6	2.00	1.74	48.69	6.29
	0.2906	1	0.3894	2	22.5	16.0	2.37	2.03	56.77	5.34
	0.2906	1	0.4188	3	25.6	18.7	2.64	2.22	62.16	4.69
	0.2906	1	0.4405	4	28.6	21.0	2.84	2.36	66.12	4.21
	0.2906	1	0.4569	5	30.9	22.9	3.00	2.47	69.22	3.83
	0.2906	1	0.4696	6	32.9	24.6	3.13	2.56	71.72	3.51
	0.2906	1	0.4795	7	34.5	26.0	3.24	2.64	73.81	3.25
	0.2906	1	0.4874	8	36.0	27.3	3.34	2.70	75.57	3.03

A1: CO₂ concentration in carbon oxide in the stream after RWReactor.

R1: Recycle ratio in the RWReactor.

A2: CO₂ concentration in carbon oxide in F1 stream.

R2: Recycle ratio in the methanol reactor.

F1: Feed gas for the methanol reactor (kgmol/h).

F2: Downstream gas in the methanol reactor (kgmol/h).

L1: Liquid product in the methanol reactor (kgmol/h).

L2: Methanol productivity (kgmol/h)

P: Purge gas (kg mol/h)